EFFECT OF HEATING RATE ON THE THERMODYNAMIC PROPERTIES OF PULVERIZED COAL

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ABSTRACT

In all major coal conversion processes, coal undergoes a devolatilization stage while it is heated to the reaction temperature. The recent experimental studies of devolatilization of pulverized coal at rapid heating rates representative of coal combustors have greatly improved our general understanding of this process. But the heat transfer analysis with commonly-applied thermal properties developed from slow heating rate experiments did not predict either the early heating prior to devolatilization or the latter stages of heating during devolatilization. Knowledge of the role of heating rate on coal thermal properties is essential to progress in advanced coal utilization technology. The objectives of this proposal are to understand the effect of heating rate on the thermal properties of pulverized coal particles. The specific objectives are to subject coal particles into a broad range of heating rates in an electrodynamic balance (10^5 - 10^7 K/s) and in a heated grid reactor (10^3 - 10^5 K/s), measure temperature histories, and develop thermal property (heat capacity and thermal conductivity) data-base for use in advanced coal combustion modeling. Experiments and modeling are being carried out to meet the project objectives. The successful accomplishment of the above goals will provide better understanding and reliable data-base for coal thermal properties for use in high heating rate applications.

Several theoretical analyses were conducted to improve the model performance of the present work and the results were compared with data available from our previous studies. Simulations using constant room temperature values for heat capacity and thermal conductivity showed excellent agreement with measurements prior to devolatilization during rapid heating (10^5 - 10^6 K/s). Increases in heat capacity and thermal conductivity observed under slow heating conditions result from bond breaking and structural changes which lead to an increase in vibrational modes of freedom in the coal structure. This suggests that under rapid heating conditions the coal structure is frozen and that these vibrational modes only become accessible at higher temperatures or longer soak times. These considerations are important if one desires to accurately model the devolatilization behavior of coals and were discussed in a paper in the journal of *Combustion and Flame* (in press).

Application of the room temperature thermal properties in the analysis, however, overpredicted the temperature measurements during devolatilization. This suggested a substantial thermophysical and thermochemical heat requirement associated with volatile evolution. A heat transfer analysis was performed to assess the magnitude of these heat requirements. Devolatilization heat requirements were treated using a lumped approach that considered the enthalpy of the volatiles leaving the particle. Excellent agreement was obtained between model projections and measurements obtained in our previous studies. This work suggests that the coal structure is initially constrained and, at high heating rates, a finite time is required for the structure to relax and respond to thermal input. This induction period may be responsible for pushing volatile evolution to higher temperatures and extending the volatile evolution time scale. A paper will be presented in this subject at the *27th International Symposium on Combustion*, August 2-7, 1998, Boulder, CO.

Measurement of temperature histories for coal particles subjected to a range of heating rates employing the electrodynamic balance measurement system discussed above and in a heated grid reactor developed by United Technologies Research Center, our industrial collaborator in this project, is in progress. Following the measurement, transport parameters tested above will be applied to predict the heated grid data. Results presented here shed some light onto the devolatilization characteristics of single bituminous coal particles under rapid heating conditions. This is important from a combustion modeling standpoint because devolatilization sets the location of the flame front. The temperature model discussed here has potential application in the future. The model can be extended to predict species concentrations of the volatiles emanating from coal particles. This will provide reliable estimation of the evolution of NO_x precursors from coal particles subjected to rapid heating during combustion process and will lead to improved designs for low emissions of nitrogen oxides.

INTRODUCTION

Devolatilization is an important initial step in virtually all commercial coal applications such as combustion, gasification, and liquefaction. The quality and yield of liquid fuels and the nature of the byproduct char derived from coal liquefaction depend on the devolatilization temperature history of the coal (heating rate), and other process variables. In coal combustion and gasification, devolatilization sets the flame front location; it also has a strong influence on product distribution (gas, liquid, tar, and char formation), soot production, and fuel-bound nitrogen and sulfur evolution.

Recent experimental studies of devolatilization of pulverized coal have greatly improved our general understanding of this process [1-4]. The role of heating rate on the onset of volatile evolution, volatile yield, product composition to a lesser extent, coal type and particle size were found to be well established. As heating becomes more rapid, the onset of devolatilization shifts to much smaller time scales and to much higher surface temperatures [1]. However, the role of heating rate on coal thermal properties was not found to be well understood.

Design of coal combustion and conversion processes require knowledge of thermal properties to construct an energy balance. The heat transfer analysis with commonly-applied thermal properties developed from slow heating rate experiments did not predict either the early heating or the latter stages of heating [2-51-3,18-19]. It is accepted that there are uncertainties in the heat capacity of coal especially for the high heating rate studies [2,4-5]. It is also accepted that the large thermal gradients within the particle (due to thermal conductivity of coal) make prediction of the temperature difficult during the early heating in these studies [2,4-5]. However, there has been no independent study conducted to investigate the effect of heating rate on the thermal properties of coal particles. Knowledge of the role of heating rate on coal thermal properties is essential to progress in advanced coal utilization technology.

The objectives of this project are to understand the effect of heating rate on thermal properties of pulverized coal particles. The specific objectives are to subject coal particles into a broad range of heating rates, measure temperature histories, and extract heat capacity and thermal conductivity information for high heating rate applications. Experiments and modeling are being carried out to meet the project objectives. The successful accomplishment of the above goals will provide better understanding and reliable data base for coal thermal properties for use in high heating rate applications.

In this paper, experimental methods and numerical analysis employed in our previous studies [6-7] and results obtained are briefly described below. Details of our current activities and future research direction in the subject matter are also presented.

EXPERIMENTAL METHODS AND NUMERICAL ANALYSIS

Single coal particles were isolated in an electrodynamic balance and their three-dimensional (external) surface areas (S_p), volumes (V_p), laser incidental areas (A_L), mass (m) and densities (ρ) were measured using rapid optical methods. The same particles were irradiated with a pulsed Nd:YAG laser beam from opposite sides. Delivered energy fluxes were selected to give heating rates on the order of 10^5 K/s. Temperature transients during heating and cooling (after the laser pulse has ended) were measured using a single-color pyrometer. Temporal intensity variations (I(t)) of individual laser pulses were followed using an ultra-fast uv light transmitter coupled to a laser monitor. Size changes were measured using a high-speed diode array imaging system. Dynamics of volatile evolution were recorded using high-speed cinematography. Details of the experimental system are presented elsewhere [2,5-7]. Experiments were performed on individual particles of PSOC 1451D hvA Pittsburgh seam bituminous coal in the aerodynamic size range of 106 - 125 µm.

During devolatilization, the volatiles evolve from within the particle, convect energy as they travel to the surface, and begin to decompose from there. With further heating, more volatiles are brought to the surface and as they decompose at the surface, mass loss is experienced. Since the intra-particle residence time of coal volatiles in small particles under high heat flux conditions will be negligible, it is assumed in the present analysis that the volatiles generated from within the particle reach the surface instantaneously and are lost at the surface. It is further assumed in the analysis that the liberating volatile mass consumes most of the heat input at the surface temperature to the extent of its instantaneous heat capacity, thus carrying away most of the thermal energy from the surface. Hence, temperature-dependent heat capacity values were assumed for the lost volatiles (C_{vol}) as they move to the surface.

With the above restrictions, the energy conservation equation including the rate of loss of thermal energy carried away by the lost volatiles at the surface temperature, T_s, is described for a volume equivalent sphere undergoing devolatilization as follows:

$$\rho_p(t) C_{pc} \frac{\partial T}{\partial t} = K_{pc} \left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) + \frac{\partial \rho_p(t)}{\partial t} \Delta H_e(T) \tag{1}$$

where the effective heat of devolatilization,

$$\Delta H_e(T) = \Delta H_d + [C_{vol} (T_s - T_\infty) - C_{pc} (T - T_\infty)] \tag{2}$$

and

$$\frac{\partial \rho_p(t)}{\partial t} = \frac{\partial (\frac{m(t)}{v})}{\partial t} \tag{3}$$

$$i.e., \quad \frac{1}{v} \frac{\partial m(t)}{\partial t} = - \frac{1}{v} k_0 \, e^{-E/RT} [m(t) - m(t_\infty)] \tag{4}$$

where m(t) is the instantaneous mass of the coal particle, and $m(t_\infty)$ is mass of the coal particle on complete devolatilization. A maximum volatility of 50% is assumed in this study for bituminous particles at rapid heating rates [1]. Thus $m(t_\infty)=0.5\ m_0$ where m_0 is the initial mass of the coal particle. k_0 and E are the first-order devolatilization kinetic parameters, the collision factor and activation energy respectively. þ is the ideal gas constant. Equation (1) represents the nonisothermal, transient process of volatile evolution of a single coal particle by accounting for the actual differences in reaction rates between the center and the surface. This approach is relevant for most practical conditions but it is generally ignored and kinetics are limited to mostly isothermal conditions.

The following boundary conditions are applied:

(i) The initial condition at t = 0:

$$T(r,0) = T_o \qquad 0 \leq r \leq R \tag{5}$$

(ii) The symmetry condition at the center r = 0:

$$\frac{\partial T(0,t)}{\partial r} = 0 \qquad t \geq 0 \tag{6}$$

(iii) The energy delivered at the surface r = R:

$$K_{pc}\,\frac{\partial T}{\partial r} = \left(\frac{2A_L \alpha I(t)}{S_p}\right) - [h(t)\,\{T_s - T_\infty\} + \sigma\,\epsilon\,\{T_s^4 - T_\infty^4\}] \tag{7}$$

The left hand-side of Equation (7) represents heat transfer to the particle interior by conduction while the first term on the right-hand side accounts for heat input by radiation, the second and third for cooling by convection and radiation respectively. The convection-conduction and radiation cooling terms were considered across the entire initial external surface area, S_p, of the particle measured prior to heating. The quantity σ is Stefan-Boltzman constant (known). The fraction of energy absorbed by the particle, α, is assumed to be equal to the fraction of energy emitted by the particle [2]. The measured transient intensity, I(t), has been used as the transient laser input flux in the source term. This input flux has been divided by a factor, $S_p/2A_L$, to account for the two-sided heating employed in the experimental system which gives a heating cross-section of $2A_L$.

Method of Solution

A numerical solution of Equation (1)was obtained using an implicit Crank-Nicholson scheme since it is a nonlinear unsteady state heat conduction problem involving the temperature to the fourth power in the third boundary condition (Equation (7)). The particle was divided into separate concentric spherical nodes and each node was assumed to be isothermal. The transient mass loss at each node was determined by employing the Badzioch kinetic equations [8]. Finally, the integrated mass loss for all the nodes is calculated at each time during devolatilization. The number of nodes was determined by trial and error. The particle was divided into more and more nodes until no difference in the computed results could be determined. Generally, 20 nodal points are used.

Model Input Parameters

Measured initial values of d_v, d_{sa}, and $S_p/2A_L$ ratio were input to the model and were assumed constant throughout the simulation. The measured density of the particle, ρ, was also input to the model. The density kept decreasing as the model calculated mass loss at each time during devolatilization. α was taken from the literature and assumed to be 0.85 for bituminous particles [2]. The room temperature heat capacity, C_{pc}, and the room temperature thermal conductivity, K_{pc}, for solid coal were input to the model. Their values are as follows: C_{pc} = 0.25 cal/g K [9], K_{pc} = 0.0005 cal/cm s K [10]. Reliable heat capacity data for coal volatiles at elevated temperatures (> 1500 K) are not available. The Merrick [9] model for the temperature-dependent heat capacity for coal was used to calculate the heat capacity of the lost volatiles. This assumption is also in line with Hertzberg et al. [11] who used Merrick's model heat capacity values in their prediction of the mass flux of volatiles emanating from the coal particles exposed to a laser beam. An apparent heat of devolatilization ($\triangle H_d$) of -250 cal/g was assumed to best predict the devolatilization temperature measurements. This value is in good agreement with the endothermic heats of carbonization reported by Kasperczyk et al. [12] and Agroskin [13] of -272 and -250 cal/g respectively.

PRIOR RESULTS AND DISCUSSIONS

Measurements were made on more than 40 coal particles. These particles were characterized as discussed above and then heated rapidly using a pulsed heating beam. Heating intensities were varied in the range from 200 to 1400 W/cm^2. In addition to changing intensities, heat pulse duration was varied from 2 to 10 ms. Property data and heating pulse information from selected particles are presented in Table 1. In the figures that follow temperature profiles from these particles are presented. These data are representative of the entire data set, which can be found in reference [5] and the discussion that follows generally applies to all of the particles in this study.

Table 1. Particle Property and Heat Flux Measurements for Selected Experiments

Particle #	d_{sa} μm	d_v μm	d_L μm	$S_p/2A_L$	ρ g/cm^3	m μg	I_{ta} W/cm^2	heating time ms
12	88	81	85	2.1	1.29	0.36	577	10
16	103	98	106	1.9	1.16	0.57	941	10
30	109	102	111	1.9	1.08	0.60	1104	2
31	123	107	125	1.9	1.20	0.77	1092	3
32	130	124	132	1.9	1.03	1.03	1017	5
36	124	116	120	2.1	1.14	0.93	1340	10

A systematic analysis was undertaken in this study in order to predict the devolatilization characteristics of single bituminous coal particles. Various model assumptions and their effect on the predicted temperature histories were critically considered. Finally, Equation 1 was arrived at as one way of modeling the temperature history of coal particles prior to and during devolatilization. Equation 1 with constant room temperature values for heat capacity and thermal conductivity predicted the measurements very well prior to devolatilization during rapid heating (see particle # 30 in Figure 1). Increases in heat capacity and thermal conductivity observed under slow heating conditions result from bond breaking and structural changes which lead to an increase in vibrational modes of freedom in the coal structure. This suggests that under rapid heating conditions the coal structure is frozen and that these vibrational modes only become accessible at higher temperatures or longer soak times. These considerations are important if one desires to accurately model the devolatilization behavior of coals and were discussed in a paper in the journal of Combustion and Flame (in press).

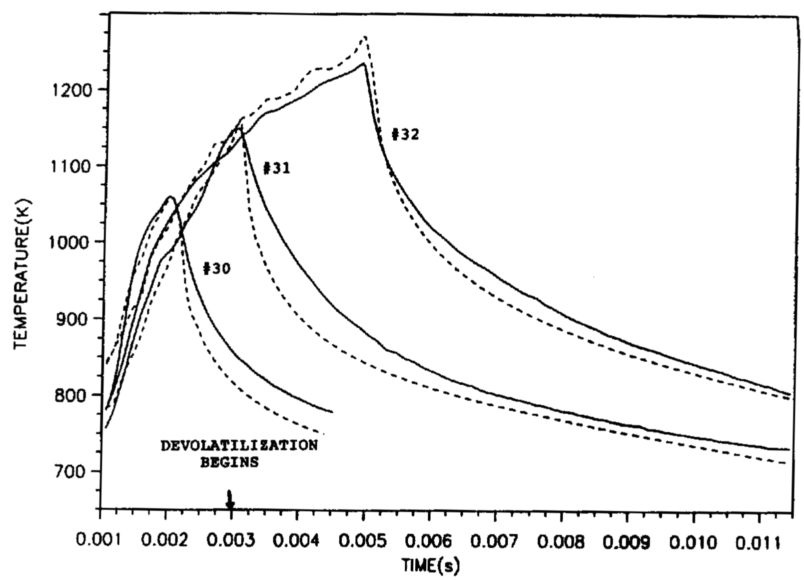

Figure 1. Comparison of Measured Temperature Histories with Projections for Several Coal Particles at Varying Heating Pulse Duration: Solid line represents measurement; Dashed line represents model projection.

During devolatilization, a substantial thermophysical and thermochemical heat requirement is associated with volatile evolution. Devolatilization heat requirements were treated using a lumped approach in equation 1 that considered the enthalpy of the volatiles leaving the particle. In Figure 1, the three particles chosen were heated at similar flux levels but the heating pulse times were varied from 2 to 5 ms. These heating conditions were selected to provide test cases for the calculation approach. In the cases of particle 31 and 32 significant volatile evolution occurred during the cooling period after truncation of the heating pulse. As illustrated, in all three cases agreement between measurement and calculation was excellent. Figure 2 illustrates additional comparisons between particle temperature measurements and model calculations during devolatilization. The temperature traces in this figure were selected to represent the range of heat flux conditions employed in this study. As illustrated, over the range of heat fluxes employed, temperature history calculations obtained using equation 1 were in excellent agreement with the measured temperature profiles. This work suggests that the coal structure is initially constrained and, at high heating rates, a finite time is required for the structure to relax and respond to thermal input. This induction period may be responsible for pushing volatile evolution to higher temperatures and extending the volatile evolution time scale. A paper will be presented in this subject at the 27th International Symposium on Combustion, August 2-7, 1998, Boulder, CO.

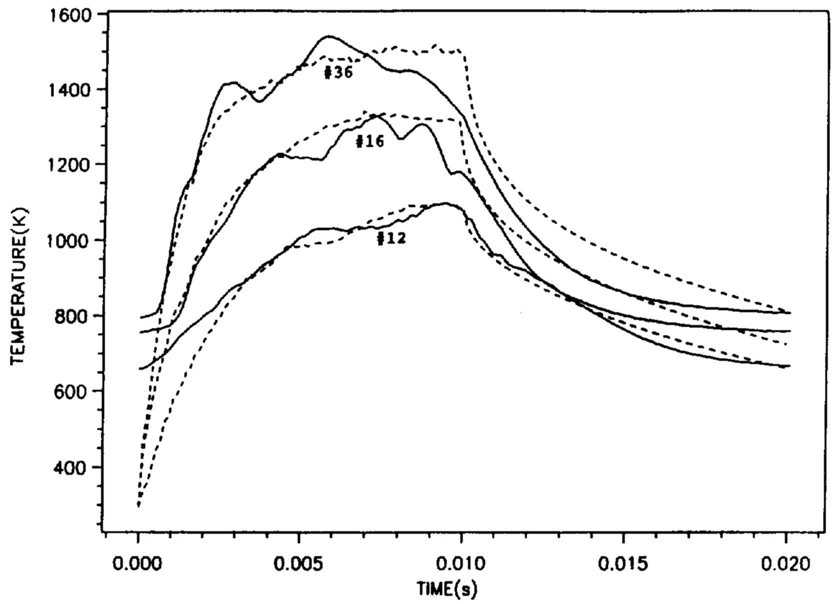

Figure 2. Comparison of Measured Temperature Histories with Model Projections for Several Coal Particles at Varying Heating Pulse Intensity: Solid line represents measurement; Dashed line represents model projection.

WORK IN PROGRESS

Measurement of temperature histories for coal particles subjected to a range of heating rates employing the electrodynamic balance measurement system discussed above and a heated grid reactor [14-15] developed by United Technologies Research Center, our industrial collaborator in a related project, is in progress. Following the measurement, transport parameters tested above will be applied to predict the heated grid data. The temperature model discussed here has potential application in the future to predict species concentrations of the volatiles emanating from coal particles. This will provide reliable estimation of the evolution of NO_x precursors from coal particles subjected to rapid heating during combustion process and will lead to improved designs for low emissions of nitrogen oxides.

SUMMARY AND CONCLUSIONS

A detailed but simple model for bituminous coal particles which accounts for particle shape, high heating rate thermal properties, kinetics, and the heat of devolatilization is discussed. The model describes the nonisothermal, transient process of volatile evolution of a single coal particle. The model predicts well the fast temperature transients characteristic of a coal particle during the entire sequence of heating, devolatilization, and cooling. The predictions of the model reproduce the main trends of the coal devolatilization process noted in previous studies. Such a model would be useful for the more efficient design of advanced coal gasifiers, combustors, and liquefaction reactors.

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NOMENCLATURE

A particle cross-sectional area (μm^2)
C particle heat capacity (cal g^{-1} K^{-1})
d particle diameter (μm)
E activation energy (cal $gmol^{-1}$)
H enthalpy (cal g^{-1})
h heat transfer coefficient at particle surface (cal s^{-1} cm^{-1} K^{-1})
I intensity of the laser (W cm^{-2})
K thermal conductivity of particle (cal s^{-1} cm^{-1} K^{-1})
k thermal diffusivity of the surrounding fluid (cm^2 s^{-1})
m particle mass (μg)
R particle radius (cm)
þ Ideal gas constant (1.987 cal $gmol^{-1}$ K^{-1})
r radial position (cm)
S surface area (μm^2)
T particle temperature (K)
t Time (s)

Greek Symbols

α particle absorptivity at 1.06 μm wavelength
∝ at infinite time
ϵ particle emissivity over the entire blackbody spectrum
σ Stefan-Boltzman constant (cal s^{-1} cm^{-2} K^{-4})
ρ particle density (g cm^{-3})

Subscripts:

0 At time = 0
d to denote devolatilization
L of laser incidental area
p of the particle
pc constant
S at particle surface
sa of surface area equivalent
v of volume equivalent
vol of coal volatiles

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